Fluorination of Plastic Containers

Summary of Information and Next Steps

1 April 2021

Scope:

- Build an understanding of: the state of the knowledge on fluorination of containers; the types of containers in the non-FIFRA space that may be treated, starting with containers for Safer-Choice-certified and other EPP products; plan for improving this knowledge through collaboration over EPA analytical work; and develop options for OPPT leadership in the fluorinated container space that may include an update to the Safer Choice standard on fluorinated containers.

The issue:

- The Public Employees for Environmental Responsibility (PEER) and the Maryland Pesticide Education Network (MPEN) discovered high level of PFAS in an insecticide widely used for public mosquito control. The insecticide is known to be Beyer Permanone 30-30.
- This pesticide is widely used by Maryland and other states in their mosquito control programs.
- PEER and MPEN notified EPA, the Maryland Department of Agriculture (MDA), and the Maryland Department of the Environment (MDE) in a letter that a sample of the pesticide Permanone 30-30, used by MDA for the state's annual mosquito control program, contains 3,500 parts per trillion (ppt) of perfluorooctanoic acid (PFOA), one of thousands of PFAS. The sample also contained approximately 630 ppt of another PFAS, hexafluoropropylene oxide dimer acid (HFPO-DA), a replacement for PFOA trademarked as GenX. [Will follow up with Thuy Nguyen to understand whether there may have been an analytical method issue with detection of GenX.]
- EPA launched an investigation over the source of the PFAS. OPP testing indicates the source is likely fluorination of the containers holding the insecticide and not the insecticide itself. The tests were largely performed on fluorinated high-density polyethylene (HDPE) barrels.

  PEER's press release: https://www.peer.org/pfas-found-in-widely-used-insecticide/

  PEER's analytical report: https://www.eenews.net/assets/2021/03/26/document_gw_01.pdf

Chemical Process

- Fluorination is primarily through reaction of the plastic container's polymers with fluorine gas (F_2) under elevated temperature and pressure. In this process, fluorine atoms replace hydrogen atoms of the polymer's methylene ($-CH_2-$) groups resulting in $-CF_2-$ groups. Possible proprietary elements of the process include the addition of oxygen gas (O_2) and likely vary among companies offering this service. Companies offering fluorination advertise degrees of fluorination – some from 1-5 and others from 1-9. Presumably the higher number indicates a higher degree of fluorination.

- Polypropylene, polyethylene, and PVC may be fluorinated because these plastics have methylene (-CH_2 -) groups. Polyethylene terephthalate (PET or PETE) does not contain methylene groups and can not be fluorinated by the method described above.
- High-density polyethylene (HDPE) carbon chain lengths are typically around $C_{2,000.}$ Shorter shorter chain impurities (C_{20+}) are common. During the fluorination process breakage in the polymer chain can lead to fluorination of the shorter chain polymer fraction and formation of PFAS impurities. OPP analysis has shown that these PFAS impurities, in the C_4 to C_{14} range, leach into rinsate.

Container types that may be fluorinated"

- HDPE is commonly used in some Safer Choice-certified product categories, including most opaque and colored traditional laundry detergent bottles and cleaning spray bottles. The EPP program also covers product categories with certified products in HDPE containers. Safer Choice does not currently collect information on PFAS in packaging. The Safer Choice standard could be modified to require information and impose restrictions.

A sample of companies that offer fluorination services:

- Berlin Packaging: [HYPERLINK "https://www.berlinpackaging.com/fluorination/"]
- Qorpak: [HYPERLINK "https://www.qorpak.com/pages/fluorination"].
- Both state the fluorination of plastic containers is needed to prevent product/air permeation through the bottle and increase bottle structural strength (add rigidity).

What has EPA done to date?

OPP

- Gathering information and performing laboratory testing.
- Launched an EPA webpage with FAQs: https://www.epa.gov/pesticides/pfas-packaging and issued a press release on 1/14/21: https://www.epa.gov/newsreleases/epa-takes-action-investigate-pfas-contamination
- Kimberly Nesci (Director, Biological and Economic Analysis Division - BEAD) is leading weekly calls to share information across the Agency; in addition to OPPT, OECA, OW, ORD and OPP are involved.
- Ed Messina and Kimberly Nesci have have had dialogue with the Ag Container Recycling Council, FDA, ACC, Crop Life, ACI, HCPA, and others.
- Thuy Nguyen (Branch Chief of BEAD's Analytical Chemistry Lab) is the lead for laboratory testing.
    - Now testing pesticide containers. Methanol is being used as a solvent rinse to extract PFOA because of its similarity to water. If PFAS leaches using methanol, it is likely that any stronger solvent will also leach PFAS from a similarly fluorinated container.
    - In fluorinated containers: finding fluorinated substances in rinsate at ppb levels.
    - In non-fluorinated containers, finding fluorinated substances at ~50 ppt (possibly from contamination from recycled content or other sources);
    - Coming next: will test containers that might be used for antimicrobial products using ethanol and surfactants to simulate a cleaning product. Such containers would be similar to containers used in Safer Choice certified products.

OPPT

- DGAD contacted OLEM so they can consider this issue within the implementation phase of their Circular Economy Strategy (first draft to be issued on Earth Day).
- DGAD met with other parts of OPPT to exchange information
- DGAD met with Mark Smith (state of Massachusetts) to hear about their testing of fluorinated containers
- DGAD now participating in OPP's weekly calls
- NCD (Traci Williamson & Tristan Butler) developed a chemistry report in which they indicate that they found new PFAS substances not on the inventory. The 40 CFR 720.30 (h)(6) article exemption applies.
- ECRMD still looking into whether there may be a SNUR violation
- Mike Garvey in OECA is leading an effort to develop a TSCA subpoena to obtain information from a barrel manufacturer.

What outside parties are doing:

- HCPA will hold a session at their spring meeting in May to learn from bottle (and other container) fluorinators; the session may be open.
- A range of organizations are testing containers for PFAS content.

Potential next steps:

Ex. 5 Deliberative Process (DP)

Other resources:

Potential substitute technology to fluorination (used in Europe for over 15 years): https://www.plasticstoday.com/barrier-plastics-launches-us-production-its-alternative-fluorinated-hdpe

Chemical Engineering News: https://cen.acs.org/environment/persistent-pollutants/Specially-treated-plastic-containers-spread/99/i9